

What is claimed is:

1. A method for producing carboxyester-modified vinylic polymeric compositions which comprises reacting in a free-radical addition polymerization reaction:

(A) about 40.0% to about 80.0% by total weight of the reactants of a monomer mixture comprising:

(1) about 15.0% to about 45.0% by total weight of the monomer mixture of a member selected from the group consisting of acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, itaconic acid, and combinations thereof,

(2) about 55.0% to about 85.0% by total weight of the monomer mixture of a member selected from the group consisting of non-carboxylic acid-containing vinylic monomers and combinations thereof,

(3) a catalytic amount of polymerization initiator, and

(4) up to about 4.0% by total weight of the monomer mixture of chain transfer agent; and

(B) about 20.0% to about 60.0% by total weight of the reactants of a mixture comprising:

(1) about 40.0% to 100.0% of at least one carboxyester formed by the condensation of at least one hydroxyl-substituted fatty acid and at least one carboxylic anhydride; and

(2) up to about 60.0% of at least one rosin;

at a temperature in the range of about 135°C to about 240°C to produce a carboxyester-modified vinylic polymeric composition having a weight average molecular weight in the range of about 4,000 to about 20,000 and an acid number in the range of about 160 to about 300.

2. The method of claim 1 which comprises reacting in a free radical addition polymerization reaction:

(A) about 40.0% to about 80.0% by total weight of the reactants of a monomer mixture comprising:

(1) about 20.0% to about 35.0% by total weight of the monomer mixture of a member selected from the group consisting of acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, itaconic acid, and combinations thereof,

(2) about 65.0% to about 80.0% by total weight of the monomer mixture of a member selected from the group consisting of non-carboxylic acid-containing vinylic monomers and combinations thereof,

(3) a catalytic amount of polymerization initiator, and

(4) up to about 2.0% by total weight of the monomer mixture of chain transfer agent; and

(B) about 20.0% to about 60.0% by total weight of the reactants of a mixture comprising:

(1) about 60.0% to 100.0% of at least one carboxyester formed by the condensation of at least one hydroxyl-substituted fatty acid and at least one carboxylic anhydride; and

(2) up to about 40.0% of at least one rosin;

at a temperature in the range of about 145°C to about 220°C to produce a carboxyester-modified vinylic polymeric composition having a weight average molecular weight in the range of about 4,000 to about 20,000 and an acid number in the range of about 160 to about 300.

3. The method of claim 1 wherein the carboxyester-modified vinylic polymer composition has a weight average molecular weight in the range of about 5,000 to about 11,000.

4. The method of claim 1 wherein the carboxyester-modified vinylic polymer composition has an acid number in the range of about 180 to about 280.

5. The method of claim 1 wherein the non-carboxylic acid-containing vinylic monomer is a member selected from the group consisting of styrene, substituted styrenes, acrylic esters, methacrylic esters, acrylamides, methacrylamides, acrylonitrile, methacrylonitrile, vinyl esters, vinyl chloride, vinylidene chloride, vinylpyridines, N-vinylamides, vinyl ethers, and combinations thereof.

6. The method of claim 5 wherein the non-carboxylic acid-containing vinylic monomer is a member selected from the group consisting of  $\alpha$ -methylstyrene, m-methylstyrene, p-methylstyrene, p-tert-butylstyrene, chlorostyrenes, 3-chloromethylstyrene, 4-chloromethylstyrene, methyl acrylate, ethyl acrylate, butyl acrylate, isobutyl acrylate, cyclohexyl acrylate, 2-ethylhexyl acrylate, isodecyl acrylate, lauryl acrylate, stearyl acrylate, isobornyl acrylate, benzyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, hydroxybutyl acrylate, methoxyethyl acrylate, ethoxyethyl acrylate, phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, glycidyl acrylate, dimethylaminoethyl acrylate, diethylaminoethyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, 2-ethylhexyl methacrylate, isodecyl methacrylate, lauryl methacrylate, stearyl methacrylate, isobornyl methacrylate, benzyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, methoxyethyl methacrylate, ethoxyethyl methacrylate, phenoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, tert-butylaminoethyl methacrylate, acetoxymethyl methacrylate, acrylamide, N-methylolacrylamide, N-butoxyethylacrylamide, N,N-dimethylacrylamide, N-isopropylacrylamide, N-tert-butylacrylamide, N-tert-octylacrylamide, diacetone acrylamide, methacrylamide, N-methylolacrylamide, N,N-dimethylacrylamide, vinyl acetate, vinyl propionate, vinyl 2-ethylhexanoate, vinyl neodecanoate, vinyl stearate, N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylformamide, N-vinylacetamide, methyl vinyl ether, ethyl vinyl ether, butyl vinyl ether, decyl vinyl ether, hydroxybutyl vinyl ether, and combinations thereof.

7. The method of claim 1 wherein the polymerization initiator comprises from about 0.2% to about 5.0% by total weight of the monomer mixture and is a member selected from the group consisting of thermal initiators, redox initiators, and combinations thereof.

8. The method of claim 1 wherein the chain transfer agent is a member selected from the group consisting of dodecyl mercaptan, mercaptoacetic acid, mercaptopropionic acid, mercaptosuccinic acid, octyl mercaptan, 2-mercaptoethanol, and combinations thereof.

9. The method of claim 1 wherein the hydroxyl-substituted fatty acid is a member selected from the group consisting of saturated carboxylic acids containing at least one carboxyl group, from one to about three hydroxyl groups, and from 8 to about 24 carbon atoms, unsaturated carboxylic acids containing at least one carboxyl group, from one to about three hydroxyl groups, and from 8 to about 24 carbon atoms, and combinations thereof.

10. The method of claim 9 wherein the hydroxyl-substituted fatty acid is a member selected from the group consisting of 12-hydroxystearic acid, ricinoleic acid, dihydroxystearic acids, aleuritic acid, and mixtures thereof.

11. The method of claim 1 wherein the hydroxyl-substituted fatty acid is 12-hydroxystearic acid.

12. The method of claim 1 wherein the carboxylic anhydride is a member selected from the group consisting of aliphatic compounds containing from one to about three cyclic anhydride groups, cycloaliphatic compounds containing from one to about three cyclic anhydride groups, aromatic compounds containing from one to about three cyclic anhydride groups, and combinations thereof.

13. The method of claim 12 wherein the carboxylic anhydride is a member selected from the group consisting of phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, benzophenonetetracarboxylic dianhydride, norbornenedicarboxylic anhydride, naphthalenedicarboxylic anhydride, succinic anhydride, alkyl-substituted succinic anhydrides, alkenyl-substituted succinic anhydrides, and mixtures thereof.

14. The method of claim 1 wherein a ratio of hydroxyl-substituted fatty acid to carboxylic anhydride in the range of about 0.3 to about 1.2 equivalents of anhydride groups per equivalent of hydroxyl groups is employed in the condensation.

5 15. The method of claim 14 wherein the ratio of hydroxyl-substituted fatty acid to carboxylic anhydride is in the range of about 0.5 to about 1.1 equivalents of anhydride groups per equivalent of hydroxyl groups.

10 16. The method of claim 1 wherein the rosin is a member selected from the group consisting of tall oil rosin, formaldehyde-treated tall oil rosin, disproportionated tall oil rosin, hydrogenated tall oil rosin, gum rosin, formaldehyde-treated gum rosin, disproportionated gum rosin, hydrogenated gum rosin, wood rosin, formaldehyde-treated wood rosin, disproportionated wood rosin, hydrogenated wood rosin, and combinations thereof.

15 17. The method of claim 1 which further comprises the addition of up to about 0.1% by total weight of the mixture of at least one bleaching agent.

18. The carboxylic acid-modified vinylic polymeric composition of claim 1.

20 19. A latex comprising as a support resin an aqueous solution of the carboxylic acid-modified vinylic polymeric composition of claim 18.

20. An ink comprising the latex of claim 19.

25 21. The ink of claim 20 wherein the ink further comprises a pigment.

22. A varnish comprising the composition of claim 18.

23. A paint comprising the latex of claim 19.

30 24. The paint of claim 23 wherein the paint further comprises a pigment.